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Prepregs for fiber composites having high strength and resilience

5 The invention relates to prepregs containing aminoplasts and intended for fiber composites having high strength and resilience, and a process for the production thereof.

10 The use of aminoplasts, such as melamine resins, for improving the crease resistance, flameproofness and rotting resistance of sheet-like textile structures comprising cellulose acetate (GB 1 164 424 A1), polyamide (JP 53 028 707 A2) or polyesters (GB 2 028 352 B2) is known.

15 The production of fiber composites from prepregs based on mats or nonwovens comprising glass fibers (US 3 574 027 A), jute fibers (JP 10 016 123 A2), ceramic fibers (JP 04 316 836 A2), asbestos fibers (DE 19 10 097 A1) or flax fibers [Hagstrand, P., Polym. Compos. (2001), 22(4), 568-578], which are impregnated with aminoplasts, such as urea resins or melamine resins, is furthermore known.

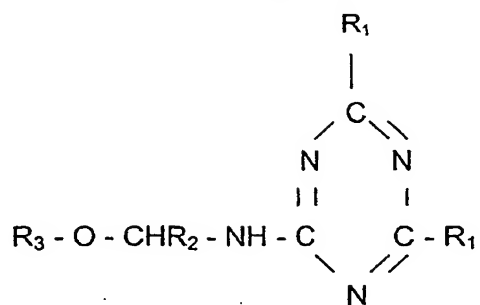
25 A disadvantage of the use of customary aminoplast laminating resins in the production of fiber composites is the unsatisfactory combination of strength and resilience properties of the composites.

30 Prepregs containing aminoplasts and intended for fiber composites which have improved strength and resilience are the aim of the invention.

35 The object of the invention was achieved by prepregs for fiber composites which, according to the invention, comprise from 50 to 85% by mass of sheet-like textile structures and from 15 to 50% by mass of polyaminotriazine ethers containing carbamic ester

groups and based on

A) aminotriazine ethers of the structure



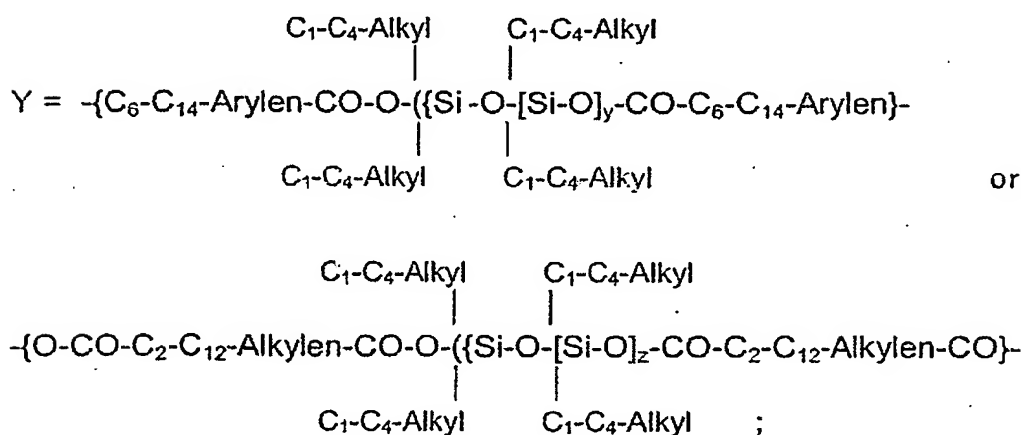
$R_1 = -NH_2, -NH-CHR_2-OH, -NH-CHR_2-O-R_3,$   
 $-NH-CHR_2-O-R_4-OH, -CH_3, -C_3H_7, -C_6H_5, -OH,$   
 phthalimido, succinimido-,  $-NH-CO-C_5-C_{18}-alkyl,$   
 $-NH-C_5-C_{18}-alkylene-OH,$   
 5  $-NH-CHR_2-O-C_5-C_{18}-alkylene-NH_2,$   
 $-NH-C_5-C_{18}-alkylene-NH_2,$

$R_2 = -H, -C_1-C_7-alkyl;$

$R_3 = -C_1-C_{18}-alkyl, -R_4-OH,$

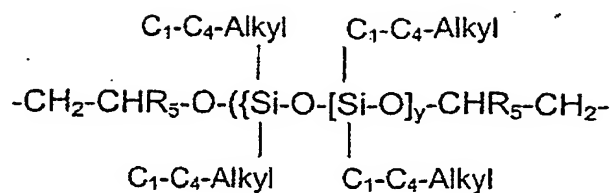
10  $R_4 = -CH(CH_3)-CH_2-O-C_2-C_{12}-alkylene-O-CH_2-CH(CH_3)-,$   
 $-CH(CH_3)-CH_2-O-C_2-C_{12}-arylene-O-CH_2-CH(CH_3)-,$   
 $-[CH_2-CH_2-O-CH_2-CH_2]_n-,$   
 $-[CH_2-CH(CH_3)-O-CH_2-CH(CH_3)]_n-,$   
 15  $-[O-CH_2-CH_2-CH_2-CH_2]_n-,$   
 $-[(CH_2)_{2-8}-O-CO-C_6-C_4-arylene-CO-O-(CH_2)_{2-8}]_n-,$   
 $-[(CH_2)_{2-8}-O-CO-C_2-C_{12}-alkylene-CO-O-(CH_2)_{2-8}]_n-,$   
 where  $n = 1$  to  $200;$

- polyester sequences of the type  
 20  $[(X)_r-O-CO-(Y)_s-CO-O(X)_r]-,$  in which  
 $X = \{(CH_2)_{2-8}-O-CO-C_6-C_{14}-arylene-CO-O-(CH_2)_{2-8}\}-$  or  
 $\{(CH_2)_{2-8}-O-CO-C_2-C_{12}-alkylene-CO-O-(CH_2)_{2-8}\}-;$



$r = 1$  to  $70;$   $s = 1$  to  $70$  and  $y = 3$  to  $50;$

25 - polyether sequences containing siloxane groups  
 and of the type



where  $R_5 = \text{H}$ ;  $\text{C}_1\text{-C}_4\text{-alkyl}$  and  $y = 3$  to  $50$ ;

- 5 - sequences based on alkylene oxide adducts of melamine of the type comprising 2-amino-4,6-di- $\text{C}_2\text{-C}_4\text{-alkyleneamino-1,3,5-triazine}$  sequences:

- phenol ether sequences based on dihydric phenols and C<sub>2</sub>-C<sub>8</sub>-diols of the type comprising -C<sub>2</sub>-C<sub>8</sub>-alkylene-O-C<sub>6</sub>-C<sub>18</sub>-arylene-O-C<sub>2</sub>-C<sub>8</sub>-alkylene sequences;

and/or

B) mixtures of from 10 to 90% by mass of aminotriazine ethers A) and from 90 to 10% by mass of polyaminotriazine ethers having molar masses of from 300 to 5000, the polyaminotriazine ethers being formed by thermal autocondensation of aminotriazine ethers A),

and

C) isocyanates of the formula R<sub>6</sub>(N = C = O)<sub>2</sub>, where R<sub>6</sub> = C<sub>6</sub>-C<sub>14</sub>-arylene, C<sub>4</sub>-C<sub>18</sub>-alkylene and/or C<sub>5</sub>-C<sub>8</sub>-cycloalkylene, and/or oligomeric polyesters or polyethers having terminal isocyanate groups and molar masses of from 200 to 5000,

the molar ratio of triazine segment to carbamic ester groups being from 1 : 1 to 1 : 4.

In the prepregs, the textile substrate materials are preferably woven fabrics or nonwovens, in particular woven fabrics or nonwovens comprising glass fibers, carbon fibers, polyamide fibers, polyester fibers, polypropylene fibers and/or thermosetting plastic fibers.

Examples of polyamide fibers of which the textile substrate materials in the prepregs may consist are fibers of polyamide-6, polyamide-6,6, polyamide-11, polyamide-12 and poly-m-phenyleneisophthalamide.

Examples of polyester fibers of which the textile substrate materials in the prepregs may consist are fibers comprising polyethylene terephthalate,

polybutylene terephthalate or poly-p-oxybenzoic acid.

Examples of thermosetting plastic fibers of which the  
textile substrate materials in the prepregs may consist  
5 are fibers comprising melamine resins or phenol resins.

In the polyaminotriazine ethers containing carbamic  
ester groups and present in the prepregs, the ratio of  
aldehyde component to triazine component is preferably  
10 from 1 : 1 to 3 : 1.

Examples of suitable aminotriazine components in the aminotriazine ethers, which are defined by the substituent  $R_1$  in the structural formula, are melamine, acetoguanamine, benzoguanamine, butyroguanamine, N-  
5 (4,6-diamino-1,3,5-triazin-2-yl)phthalimide and 2,4-diamino-6-succinimido-1,3,5-triazine.

Examples of suitable  $C_1$ - $C_8$ -aldehyde components in the aminotriazine ethers, which are defined by the  
10 substituent  $R_2$  in the structural formula, are formaldehyde, acetaldehyde and trimethylolacetaldehyde.

The aminotriazine ethers as a basis for the polyaminotriazine ethers containing carbamic ester  
15 groups in the prepreg can be prepared by reaction of aminotriazines with  $C_1$ - $C_8$ -aldehydes to give aminotriazine precondensates, etherification of the aminotriazine precondensates with  $C_1$ - $C_4$ -alcohols, and optionally subsequent transesterification with  $C_5$ - $C_{18}$ -  
20 alcohols and/or diols of the type  $HO-R_4-OH$ . In the structural formula, the etherification component, which is a  $C_1$ - $C_{18}$ -alcohol and/or a diol of the type  $HO-R_4-OH$ , is defined by  $R_3$ .

25 Examples of  $C_1$ - $C_4$ -alcohols which may be present as etherification component  $R_3$  in the aminotriazine ethers are methanol, isopropanol and butanol.

Examples of  $C_5$ - $C_{18}$ -alcohols which may be present as  
30 etherification component  $R_3$  in the aminotriazine ethers are ethylhexyl alcohol, dodecyl alcohol and stearyl alcohol.

Examples of diols of the type  $HO-R_4-OH$ ,  $R_4 = C_2$ - $C_{18}$ -alkylene, which may be present as etherification  
35 component  $R_3$  in the aminotriazine ethers are ethylene glycol, butanediol, octanediol, dodecanediol and octadecanediol.

Examples of diols of the type  $\text{HO-R}_4\text{-OH}$ ,  $\text{R}_4 =$   
- $[\text{CH}_2\text{-CH}(\text{CH}_3)\text{-O-CH}_2\text{-CH}(\text{CH}_3)]_n$ - and  $n = 1\text{-}200$ , which may  
be present as etherification component  $\text{R}_3$  in the  
5 aminotriazine ethers are polyethylene glycols having  
molar masses of from 500 to 5000.



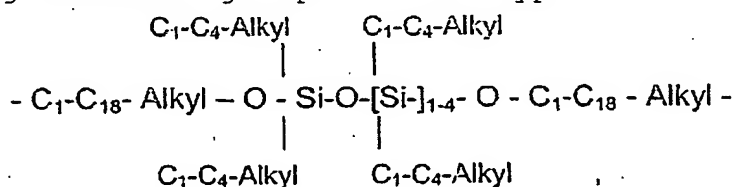
Examples of diols of the type HO-R<sub>4</sub>-OH, R<sub>4</sub> = -[O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>]<sub>n</sub>- and n = 1-200, which may be present as etherification component R<sub>3</sub> in the aminotriazine ethers are polypropylene glycols having molar masses of from 500 to 5000.

Examples of diols of the type HO-R<sub>4</sub>-OH, R<sub>4</sub> = -[O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>]<sub>n</sub>- and n = 1-200, which may be present as etherification component R<sub>3</sub> in the aminotriazine ethers are polytetrahydrofurans having molar masses of from 500 to 5000.

Examples of diols of the type HO-R<sub>4</sub>-OH, R<sub>4</sub> = -[(CH<sub>2</sub>)<sub>2-8</sub>-O-CO-C<sub>6</sub>-C<sub>14</sub>-arylene-CO-O-(CH<sub>2</sub>)<sub>2-8</sub>]<sub>n</sub>-, which may be present as etherification component R<sub>3</sub> in the aminotriazine ethers are esters and polyesters based on saturated dicarboxylic acids, such as terephthalic acid, isophthalic acid or naphthalenedicarboxylic acid, and diols, such as ethylene glycol, butanediol, neopentylglycol and/or hexanediol. A preferred ester is bis(hydroxyethyl) terephthalate.

Examples of diols of the type HO-R<sub>4</sub>-OH, R<sub>4</sub> = -[(CH<sub>2</sub>)<sub>2-8</sub>-O-CO-C<sub>2</sub>-C<sub>12</sub>-alkylene-CO-O-(CH<sub>2</sub>)<sub>2-8</sub>]<sub>n</sub>-, which may be present as etherification component R<sub>3</sub> in the aminotriazine ethers are polyesters based on saturated dicarboxylic acids, such as adipic acid and/or succinic acid, unsaturated dicarboxylic acids, such as maleic acid, fumaric acid and/or itaconic acid, and diols, such as ethylene glycol, butanediol, neopentylglycol and/or hexanediol.

Examples of diols of the type HO-R<sub>4</sub>-OH, R<sub>4</sub> = sequences containing siloxane groups of the type



which may be present as etherification component  $R_3$  in the aminotriazine ethers are 1,3-bis(hydroxybutyl)-tetramethyldisiloxane and 1,3-bis(hydroxyoctyl)-tetraethyldisiloxane.

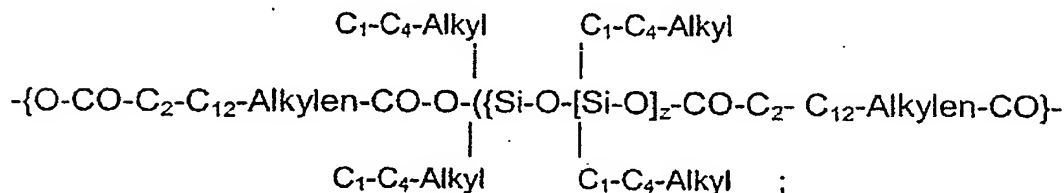
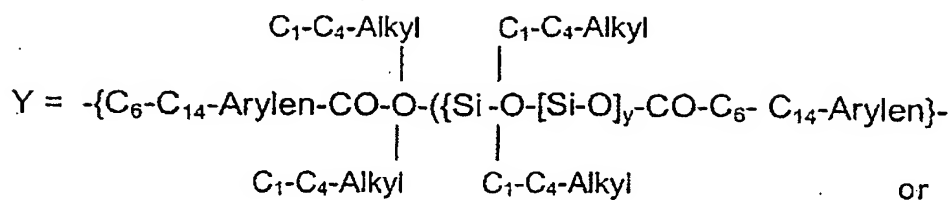
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Examples of polyester sequences comprising diols containing siloxane groups of the type  $\text{HO-R}_4\text{-OH}$ ,  $R_4 = -[(X)_r\text{-O-CO-(Y)}_s\text{-CO-O-(X)}_r]\text{-}$ , which may be present as etherification component  $R_3$  in the aminotriazine ethers,

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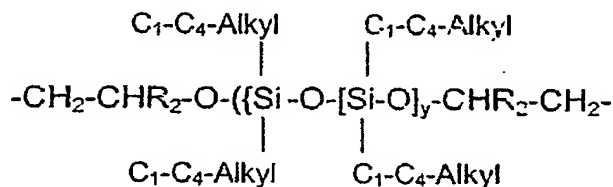
in which

$X = -[(\text{CH}_2)_{2-8}\text{-O-CO-C}_6\text{-C}_{14}\text{-arylene-CO-O-(CH}_2)_{2-8}]\text{-}$  or  
 $-[(\text{CH}_2)_{2-8}\text{-O-CO-C}_2\text{-C}_{12}\text{-alkylene-CO-O-(CH}_2)_{2-8}]\text{-};$



$r = 1$  to  $70$ ;  $s = 1$  to  $70$  and  $y = 3$  to  $50$ ;  
 are polyesters containing hydroxyl end groups and based  
 5 on aromatic  $\text{C}_6\text{-C}_{14}$ -arylenedicarboxylic acids, such as  
 terephthalic acid or naphthalenedicarboxylic acid,  
 aliphatic  $\text{C}_2\text{-C}_{12}$ -alkylenedicarboxylic acids, such as  
 adipic acid, maleic acid or pimelic acid, diols, such  
 as ethylene glycol, butanediol, neopentylglycol or  
 10 hexanediol, and siloxanes, such as hexamethyldisiloxane  
 or  $\alpha,\omega$ -dihydroxypolydimethylsiloxane.

Examples of polyetherdiols  $\text{HO-R}_4\text{-OH}$  containing siloxane  
 groups,  $\text{R}_4$  = polyether sequences of the type



15

where  $\text{R}_2 = \text{H}$ ;  $\text{C}_1\text{-C}_4$ -alkyl and  $y = 3$  to  $50$ ;  
 which may be present as etherification component  $\text{R}_3$  in  
 the aminotriazine ethers are polyetherdiols based on  
 siloxanes, such as hexamethyldisiloxane or  $\alpha,\omega$ -  
 20 dihydroxypolydimethylsiloxane, and alkylene oxides,  
 such as ethylene oxide or propylene oxide.

Examples of diols based on alkylene oxide adducts of

melamine of the type 2-amino-4,6-bis(hydroxy-C<sub>2</sub>-C<sub>4</sub>-alkyleneamino)-1,3,5-triazine which may be present as etherification component R<sub>3</sub> in the aminotriazine ethers are diols based on melamine and ethylene oxide or  
5 propylene oxide.

Examples of phenol ether diols based on dihydric phenols and C<sub>2</sub>-C<sub>8</sub>-diols of the bis(hydroxy-C<sub>2</sub>-C<sub>8</sub>-alkylene-O-)C<sub>6</sub>-C<sub>18</sub>-arylene type which may be present as

etherification component  $R_3$  in the aminotriazine ethers are ethylene oxide adducts or propylene oxide adducts of diphenylolpropane.

5 In addition to diols as polyhydric alcohols, trihydric alcohols, such as glycerol, or tetrahydric alcohols, such as erythritol, or mixtures thereof with dihydric alcohols may be present as etherification component  $R_3$  in the aminotriazine ethers.

10

A preferred process for the preparation of polyaminotriazine ethers having molar masses of from 300 to 5000 as a basis for the polyaminotriazine ethers containing carbamic ester groups in the preregs is the  
15 thermal autocondensation of the aminotriazine ethers in continuous kneaders at from 120 to 220°C.

In the preregs, the polyaminotriazine ethers containing carbamic ester groups are preferably  
20 polyaminotriazine ethers based on melamine, formaldehyde, methanol and diisocyanates of the type  $R_6(N = C = O)_2$ .

Examples of isocyanates of the formula  $R_6(N = C = O)_2$  as  
25 the isocyanate component in the polytriazine ethers containing carbamic ester groups are tetramethylene diisocyanate, hexamethylene diisocyanate, decamethylene diisocyanate, diphenylmethane diisocyanate, p-toluene diisocyanate or diisocyanatodiphenyl ether.

30

Preferred polyaminotriazine ethers containing carbamic ester groups are in particular polyaminotriazine ethers based on

35 B) mixtures of from 5 to 30% by mass of aminotriazine ethers A) and from 95 to 70% by mass of polyaminotriazine ethers having molar masses of from 300 to 5000, the polyaminotriazine ethers being formed by thermal autocondensation of aminotriazine

ethers A),

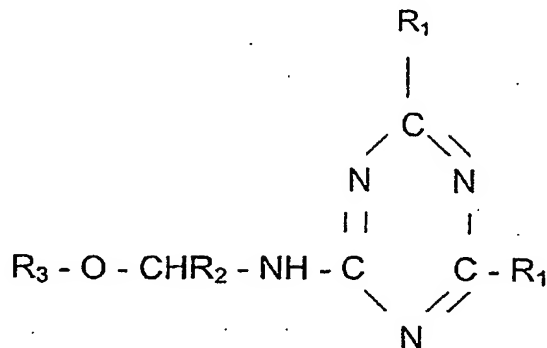
and

- 5 C) isocyanates of the formula  $R_6(N = C = O)_2$ , where  
 $R_4 = C_4-C_{18}$ -alkylene and/or  $C_5-C_8$ -cycloalkylene,  
and/or oligomeric polyesters or polyethers  
10 having terminal isocyanate groups and molar  
masses of from 200 to 5000.

The prepregs for fiber composites having high strength  
and resilience are produced by a process in which,  
10 according to the invention, prepregs which comprise  
from 50 to 85% by mass of sheet-like textile structures  
and from 15 to 50% by mass of polyaminotriazine ethers

containing carbamic ester groups are produced by a melt application method in which mixtures of

A) aminotriazine ethers having the structure



5

$R_1 = -NH_2, -NH-CHR_2-OH, -NH-CHR_2-O-R_3,$   
 $-NH-CHR_2-O-R_4-OH, -CH_3, -C_3H_7, -C_6H_5, -OH,$   
 phthalimido, succinimido,  $-NH-CO-C_5-C_{18}\text{-alkyl},$   
 $-NH-C_5-C_{18}\text{-alkylene-OH},$   
 $-NH-CHR_2-O-C_5-C_{18}\text{-alkylene-NH}_2,$   
 $-NH-C_5-C_{18}\text{-alkylene-NH}_2,$

10

$R_2 = -H, -C_1-C_7\text{-alkyl};$   
 $R_3 = -C_1-C_{18}\text{-alkyl}, -R_4-OH,$

15

$R_4 = -CH(CH_3)-CH_2-O-C_2-C_{12}\text{-alkylene-O-CH}_2-CH(CH_3)-,$   
 $-CH(CH_3)-CH_2-O-C_2-C_{12}\text{-arylene-O-CH}_2-CH(CH_3)-,$   
 $-[CH_2-CH_2-O-CH_2-CH_2]_n-,$   
 $-[CH_2-CH(CH_3)-O-CH_2-CH(CH_3)]_n-,$   
 $-[O-CH_2-CH_2-CH_2-CH_2]_n-,$   
 $-[(CH_2)_{2-8}-O-CO-C_6-C_{14}\text{-arylene-CO-O-(CH}_2)_{2-8}]_n-,$   
 $-[(CH_2)_{2-8}-O-CO-C_2-C_{12}\text{-alkylene-CO-O-(CH}_2)_{2-8}]_n-,$   
 where  $n = 1$  to 200;

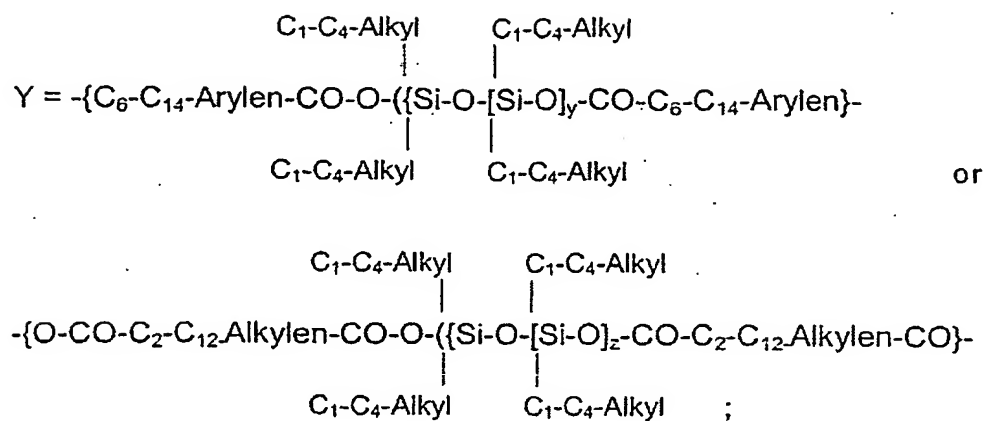
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- polyester sequences containing siloxane groups  
 of the type  $-[(X)_r-O-CO-(Y)_s-CO-O-(X)_r]-,$

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in which

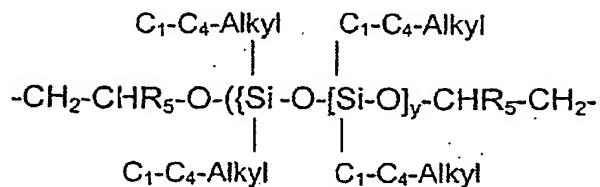
$X = -\{(CH_2)_{2-8}-O-CO-C_6-C_{14}\text{-arylene-CO-O-(CH}_2)_{2-8}\}-$  or  
 $-\{(CH_2)_{2-8}-O-CO-C_2-C_{12}\text{-alkylene-CO-O-(CH}_2)_{2-8}\}-;$





$r = 1$  to  $70$ ;  $s = 1$  to  $70$  and  $y = 3$  to  $50$ ;

- polyether sequences containing siloxane groups of the type



where  $R_5 = \text{-H}$ ;  $\text{-C}_1\text{-C}_4\text{-alkyl}$  and  $y = 3$  to  $50$ ;

- sequences based on alkylene oxide adducts of melamine of the type comprising 2-amino-4,6-di- $\text{C}_2\text{-C}_4\text{-alkyleneamino-1,3,5-triazine}$  sequences:

- phenol ether sequences based on dihydric phenols and  $\text{C}_2\text{-C}_8\text{-diols}$  of the type comprising  $\text{-C}_2\text{-C}_8\text{-alkylene-O-C}_6\text{-C}_{18}\text{-arylene-O-C}_2\text{-C}_8\text{-alkylene}$  sequences;

and/or

B) mixtures of from  $10$  to  $90\%$  by mass of aminotriazine ethers A) and from  $90$  to  $10\%$  by mass of polyaminotriazine ethers having molar masses of from  $300$  to  $5000$ , the polyaminotriazine ethers being formed by thermal autocondensation of aminotriazine ethers A), and

C) isocyanates of the formula  $R_6(\text{N}=\text{C}=\text{O})_2$ , where  $R_6 = \text{C}_6\text{-C}_{14}\text{-arylene}$ ,  $\text{C}_4\text{-C}_{18}\text{-alkylene}$  and/or  $\text{C}_5\text{-C}_8\text{-cycloalkylene}$ , and/or oligomeric polyesters or polyethers having terminal isocyanate groups and molar masses of from  $200$  to  $5000$ ,

the molar ratio of diisocyanate to the sum of imino groups and amino groups in the triazine sequence being from  $0.15 : 1$  to  $0.65 : 1$ , and it being possible for the mixtures to contain from  $0.05$  to  $2\%$  by mass, based on the aminotriazine ethers, of latent curing agents,

are melted at temperatures of from 85 to 130°C, reacted, and applied to the textile substrate materials.

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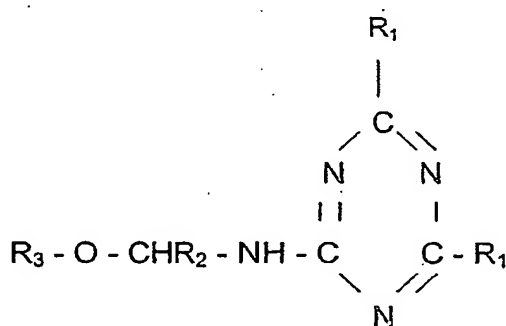
Mixtures which predominantly comprise aminotriazine ethers and diisocyanates can be applied to the moving sheet-like web during the melt application method by applying the low-viscosity melt by means of a knife  
10 coater or by spraying on.

Extrusion coating units are suitable in the melt application method for melting and applying relatively high-viscosity mixtures which predominantly comprise polyaminotriazine ethers and diisocyanates.

5

A second process for the production of prepregs for fiber composites having high strength and resilience comprises producing the prepregs according to the invention, which comprise from 50 to 85% by mass of  
 10 sheet-like textile structures and from 15 to 50% by mass of polyaminotriazine ethers containing carbamic ester groups, by a liquid application method, in which dispersions in C<sub>5</sub>-C<sub>12</sub>-hydrocarbons and/or C<sub>3</sub>-C<sub>12</sub>-ketones or solutions in dimethyl sulfoxide, dimethylformamide  
 15 and/or dimethylacetamide, having a solids content of 25 to 70% by mass, comprising

A) aminotriazine ethers of the structure



- 20  $R_1 = -NH_2, -NH-CHR_2-OH, -NH-CHR_2-O-R_3,$   
 $-NH-CHR_2-O-R_4-OH, -CH_3, -C_3H_7, -C_6H_5, -OH,$   
 phthalimido, succinimido,  $-NH-CO-C_5-C_{18}\text{-alkyl},$   
 $-NH-C_5-C_{18}\text{-alkylene-OH},$   
 $-NH-CHR_2-O-C_5-C_{18}\text{-alkylene-NH}_2,$   
 25  $-NH-C_5-C_{18}\text{-alkylene-NH}_2,$

$R_2 = -H, -C_1-C_7\text{-alkyl};$

$R_3 = -C_1-C_{18}\text{-alkyl}, -R_4-OH,$

- 30  $R_4 = -CH(CH_3)-CH_2-O-C_2-C_{12}\text{-alkylene-O-CH}_2-CH(CH_3)-,$   
 $-CH(CH_3)-CH_2-O-C_2-C_{12}\text{-arylene-O-CH}_2-CH(CH_3)-,$   
 $-[CH_2-CH_2-O-CH_2-CH_2]_n-,$

- 5
- [CH<sub>2</sub>-CH(CH<sub>3</sub>)-O-CH<sub>2</sub>-CH(CH<sub>3</sub>)]<sub>n</sub>-,
  - [O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>]<sub>n</sub>-,
  - [(CH<sub>2</sub>)<sub>2-8</sub>-O-CO-C<sub>6</sub>-C<sub>14</sub>-arylene-CO-O-(CH<sub>2</sub>)<sub>2-8</sub>]<sub>n</sub>-,
  - [(CH<sub>2</sub>)<sub>2-8</sub>-O-CO-C<sub>2</sub>-C<sub>12</sub>-alkylene-CO-O-(CH<sub>2</sub>)<sub>2-8</sub>]<sub>n</sub>-,
- where n = 1 to 200;
- polyester sequences containing siloxane groups  
of the type -[(X)<sub>r</sub>-O-CO-(Y)<sub>s</sub>-CO-O-(X)<sub>r</sub>]-,

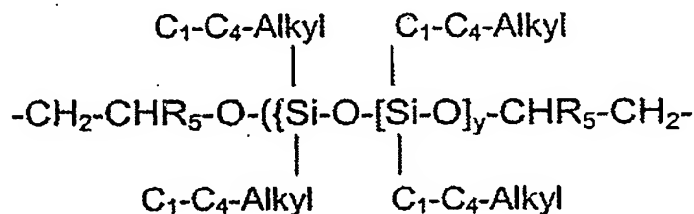
in which

$X = -\{(CH_2)_{2-8}-O-CO-C_6-C_{14}-\text{arylene}-CO-O-(CH_2)_{2-8}\}-$  or  
 $-\{(CH_2)_{2-8}-O-CO-C_2-C_{12}-\text{alkylene}-CO-O-(CH_2)_{2-8}\}-;$

$Y = -\{C_6-C_{14}-\text{Arylen}-CO-O-\overset{\overset{C_1-C_4\text{-Alkyl}}{|}}{\underset{\underset{C_1-C_4\text{-Alkyl}}{|}}{\{Si-O-[Si-O]_y-CO-C_6-C_{14}-\text{Arylen}\}}}-$   
or

$-\{O-CO-C_2-C_{12}-\text{Alkylene}-CO-O-\overset{\overset{C_1-C_4\text{-Alkyl}}{|}}{\underset{\underset{C_1-C_4\text{-Alkyl}}{|}}{\{Si-O-[Si-O]_z-CO-C_2-C_{12}-\text{Alkylene}-CO\}}}-$   
;

- 5  $r = 1$  to  $70$ ;  $s = 1$  to  $70$  and  $y = 3$  to  $50$ ;  
 - polyether sequences containing siloxane groups of the type



where  $R_5 = -H$ ;  $-C_1-C_4\text{-alkyl}$  and  $y = 3$  to  $50$ ;

- 10 - sequences based on alkylene oxide adducts of melamine of the type comprising 2-amino-4,6-di- $C_2-C_4\text{-alkyleneamino-1,3,5-triazine}$  sequences:  
 - phenol ether sequences based on dihydric phenols and  $C_2-C_8\text{-diols}$  of the type comprising  $-C_2-C_8\text{-alkylene-O-C}_6\text{-C}_{18}\text{-arylene-O-C}_2\text{-C}_8\text{-alkylene}$  sequences;

and/or

- 20 B) mixtures of from 10 to 90% by mass of aminotriazine ethers A) and from 90 to 10% by mass of polyaminotriazine ethers having molar masses of from 300 to 5000, the polyaminotriazine ethers being formed by autocondensation of triazine  
 25 ethers A), and

C) isocyanates of the formula  $R_6(N = C = O)_2$ ,  
where  $R_6 = -C_6-C_{14}$ -arylene,  $-C_4-C_{18}$ -alkylene and/or  
-C<sub>5</sub>-C<sub>8</sub>-cycloalkylene, and/or oligomeric polyesters  
5 or polyethers having terminal isocyanate groups  
and molar masses of from 200 to 5000,

the molar ratio of diisocyanate to the sum of imino groups and amino groups in the triazine sequence being from 0.15 : 1 to 0.65 : 1, and it being possible for the mixtures to contain from 0.05 to 2% by mass, based on the aminotriazine ethers, of latent curing agents, are brought into contact at temperatures from 5 to 80°C with the textile substrate materials and reacted at from 80 to 120°C/from 0.1 to 1 bar and dried.

Examples of C<sub>5</sub>-C<sub>12</sub>-hydrocarbons which can be used as dispersants in the liquid application method are pentane, isooctane and dodecane.

Examples of C<sub>3</sub>-C<sub>12</sub>-ketones which can be used as dispersants in the liquid application method are methyl ethyl ketone, diisobutyl ketone and ethyl hexyl ketone.

In the melt application method and in the liquid application method for the production of prepregs, 2,4,6-tris(methoxymethylamino)-1,3,5-triazine is preferably used as the aminotriazine ether.

In the melt application method and in the liquid application method for the production of prepregs, the latent curing agents used are preferably weak acids, in particular

- blocked sulfonic acids,
- alkali metal salts or ammonium salts of phosphoric acid,
- C<sub>1</sub>-C<sub>12</sub>-alkyl esters or C<sub>2</sub>-C<sub>8</sub>-hydroxyalkyl esters of aromatic C<sub>6</sub>-C<sub>14</sub>-carboxylic acids or inorganic acids,
- salts of melamine or guanamines with aliphatic C<sub>1</sub>-C<sub>18</sub>-carboxylic acids,
- anhydrides, monoesters or monoamides of C<sub>4</sub>-C<sub>20</sub>-dicarboxylic acids,
- monoesters or monoamides of copolymers of

- ethylenically unsaturated C<sub>4</sub>-C<sub>20</sub>-dicarboxylic anhydrides and ethylenically unsaturated monomers of the type comprising C<sub>2</sub>-C<sub>20</sub>-olefins and/or C<sub>8</sub>-C<sub>20</sub>-vinylaromatics, and/or
- 5 - salts of C<sub>1</sub>-C<sub>12</sub>-alkylamines or alkanolamines with aliphatic C<sub>1</sub>-C<sub>18</sub>-carboxylic acids, aromatic C<sub>6</sub>-C<sub>14</sub>-carboxylic acids or alkylaromatic carboxylic acids and inorganic acids of the hydrochloric acid, sulfuric acid or phosphoric
- 10 acid type.



- Examples of blocked sulfonic acids which can be used as latent curing agents in the production of preregs are benzil monooxime tosylate, ethyl  $\alpha$ -cyclohexylsulfonyl-oxyiminophenylacetate, acetone oxime p-benzoylbenzenesulfonate,  $\alpha$ -(4-nitrobenzenesulfonyloxy-imino)benzyl cyanide, 2-nitrobenzyl sulfonate and 2-methylsulfonyloxyimino-4-phenylbut-3-ene nitrile.
- 10 Examples of aliphatic C<sub>4</sub>-C<sub>18</sub>-carboxylic acids which can be used as latent curing agents in the production of the preregs are butyric acid, caproic acid, palmitic acid, stearic acid and oleic acid.
- 15 Examples of alkali metal salts or ammonium salts of phosphoric acid which can be used as latent curing agents in the production of preregs are ammonium hydrogen phosphate, sodium polyphosphate and potassium hydrogen phosphate.
- 20 Examples of C<sub>1</sub>-C<sub>12</sub>-alkyl esters or C<sub>2</sub>-C<sub>8</sub>-hydroxyalkyl esters of aromatic C<sub>6</sub>-C<sub>14</sub>-carboxylic acids or inorganic acids which can be used as latent curing agents in the production of the preregs are dibutyl phthalate, diglycol phthalate and/or glycol trimellitate.
- 25 Examples of salts of melamine or guanamines with aliphatic C<sub>1</sub>-C<sub>18</sub>-carboxylic acids which can be used as latent curing agents in the production of the preregs are melamine formate, melamine citrate and/or acetoguanamine butyrate.
- 30 Examples of anhydrides, monoesters or monoamides of C<sub>4</sub>-C<sub>20</sub>-dicarboxylic acids which can be used as latent curing agents in the production of the preregs are maleic anhydride, mono-C<sub>1</sub>-C<sub>18</sub>-alkyl maleates, such as monobutyl maleate, monoethylhexyl maleate or monostearyl maleate, or mono-C<sub>1</sub>-C<sub>18</sub>-alkylmaleamides, such as monoethyl maleamide, monooctyl maleamide or

monostearylmaideamide.

Examples of monoesters or monoamides of copolymers of  
ethylenically unsaturated C<sub>4</sub>-C<sub>20</sub>-dicarboxylic anhydrides  
5 and ethylenically unsaturated monomers of the type  
comprising C<sub>2</sub>-C<sub>20</sub>-olefins and/or C<sub>8</sub>-C<sub>20</sub>-vinylaromatics  
which can be used as latent curing agents in the  
production of the prepregs are monoesters or monoamides  
of copolymers of maleic anhydride and C<sub>3</sub>-C<sub>8</sub>- $\alpha$ -olefins of  
10 the type comprising isobutene, diisobutene and/or 4-

methylopentene and/or styrene having a molar ratio of maleic anhydride to C<sub>3</sub>-C<sub>8</sub>- $\alpha$ -olefin or styrene or corresponding monomer mixtures of from 1 : 1 to 1 : 5.

- 5 Examples of salts of C<sub>1</sub>-C<sub>12</sub>-alkylamines or alkanolamines with aliphatic C<sub>1</sub>-C<sub>18</sub>-carboxylic acids, aromatic C<sub>6</sub>-C<sub>14</sub>-carboxylic acids or alkylaromatic carboxylic acids and inorganic acids of the hydrochloric acid, sulfuric acid or phosphoric acid type which can be used as latent  
10 curing agents in the production of the preregs are ethanolanmonium chloride, triethylanmonium maleate, diethanolanmonium phosphate and/or isopropylanmonium p-toluenesulfonate.
- 15 Fiber composites which are produced using the preregs described above are furthermore according to the invention.

For the production of the fiber composites, the preregs which comprise from 50 to 85% by mass of  
20 sheet-like textile structures and from 15 to 50% by mass of polyaminotriazine ethers containing carbamic ester groups can be cured at temperatures of from 135°C to 190°C and in residence times of from 4 to 90 min in the form of a single layer or a plurality of layers,  
25 preferably in presses at from 40 to 120 bar.

The curing of the preregs at temperatures of from 135°C to 190°C and in residence times of from 4 to 90 min can also be effected after lamination of the  
30 preregs which comprise from 50 to 85% by mass of sheet-like textile structures and from 15 to 50% by mass of polyaminotriazine ethers containing carbamic ester groups with sheet-like substrate materials comprising wood, metal, plastic, paper, board, sheet-  
35 like textile structures or preregs based on substrate materials, such as sheet-like textile structures or paper, which are impregnated with laminating resins, such as epoxy resins, phenol resins or unsaturated polyester resins, preferably in presses with shaping

and from 40 to 120 bar.

Examples of sheet-like substrate materials which can be used in the production of fiber composites by lamination with prepregs comprising from 50 to 85% by mass of sheet-like textile structures and from 15 to 50% by mass of polyaminotriazine ethers containing carbamic ester groups are copper foils, kraft paper prepregs, polystyrene foam, polyolefin foam, metal nets and phenol resin/glass fiber prepregs.

The fiber composites according to the invention are preferably suitable for use as heat protection clothing, fire protection blankets, electrical insulation papers, flameproofed components in electronics, construction parts and vehicle fittings.

The invention is explained by the following examples:

#### Example 1

10

##### 1.1 Preparation of the mixture of aminotriazine ether and polyaminotriazine ether

15 A melamine dispersion is prepared in a 30 l stirred autoclave by introducing 1.0 kg of melamine in 13.7 kg of methanol at 95°C and, after the pH has been adjusted to 6, a mixture of 3 kg of formaldehyde, 1.29 kg of methanol and 4.31 kg of water, which is preheated to 90°C, is metered under pressure into the stirred  
20 autoclave as the aldehyde component, and the reaction mixture is reacted at a reaction temperature of 95°C and in a reaction time of 5 min.

25 After cooling to 65°C, a pH of 9 is established by adding N/10 sodium hydroxide solution, and the etherified aminotriazine resin condensate dissolved in the water-methanol mixture is transferred, after addition of 2.23 kg of butanol, into a first vacuum evaporator, in which the solution of the etherified  
30 aminotriazine resin condensate is concentrated at 80°C to give a highly concentrated aminotriazine resin solution which has a solids content of 75% by mass and a butanol content of 10% by mass.

35 The highly concentrated solution of the etherified aminotriazine resin is subsequently transferred to a second vacuum evaporator and concentrated at 90°C to give a syrupy melt which has a solids content of 95% by mass and a butanol content of 5% by mass.

1.2 Production of the prepreg and pressing to give the fiber composite

- 5 The syrupy melt is metered at 2.6 kg/h into the feed hopper of a GL 27 D44 (Leistritz) laboratory extruder having vacuum devolatilization zones after the feed zone and before the product discharge, sidestream metering for liquid media and 100 x 2 mm flat sheet  
10 die, temperature profile 180°C/220°C/220°C/220°C/200°C/170°C/140°C/ 110°C/90°C/90°C/90°C,

extruder speed  $200 \text{ min}^{-1}$ , the aminotriazine ether is subjected to thermal condensation and the volatile fractions are removed by devolatilization at 100 mbar.

The analysis sample of aminotriazine ether/polyamino-  
5 triazine ether mixture taken from the vacuum devolatilization nozzle has a molar mass of 650.

2.25 kg/h of hexamethylene diisocyanate are metered into the melt of the polyaminotriazine ether/amino-  
10 triazine ether mixture by means of sidestream metering and homogenized with the mixture. After a second vacuum devolatilization at 150 mbar, the melt is extruded through the flat sheet die onto a glass fiber fabric moving at 5 m/min (mass per unit area  $200 \text{ g/m}^2$ ), which fabric passes through a heating tunnel ( $120^\circ\text{C}$ , average  
15 residence time 8 min) after the impregnation.

The impregnated glass fiber fabric has a resin content of 44% by mass. ATR investigations give a ratio of triazine segment to carbamic ester groups of 1:2.6.

20

The impregnated glass fiber fabric is pressed in a press at  $160^\circ\text{C}/30 \text{ bar}$  for 20 min with curing.

The laminate has the following material  
25 characteristics:

Flexural strength:  $320 \text{ N/mm}^2$  Impact strength:  $78 \text{ kJ/m}^2$   
Tensile strength:  $180 \text{ N/mm}^2$  Elongation: 3%.

If a laminate having the same resin content is produced  
30 under analogous conditions but without addition of the diisocyanate, the following material characteristics are obtained:

Flexural strength:  $290 \text{ N/mm}^2$  Impact strength:  $52 \text{ kJ/m}^2$   
Tensile strength:  $168 \text{ N/mm}^2$  Elongation: 2.2%.

35

Example 2

2.1 Preparation of the aminotriazine ether

An aminotriazine dispersion is prepared in a 30 l stirred autoclave by introducing 0.9 kg of melamine and 0.1 kg of benzoguanamine in 15 kg of methanol at 95°C and, after the pH has been adjusted to 6.2, a mixture  
5 of 2.7 kg of formaldehyde, 0.3 kg of glyoxal and 3 kg of water, which is preheated to 90°C, is metered under pressure into the stirred autoclave as



the aldehyde component, and the reaction mixture is reacted at a reaction temperature of 90°C and in a reaction time of 10 min.

5 After cooling to 65°C, a pH of 9.2 is established by adding N/10 sodium hydroxide solution, and the etherified aminotriazine resin condensate dissolved in the water-methanol mixture is transferred, after addition of 0.6 kg of butanol, into a first vacuum  
10 evaporator, in which the solution of the etherified aminotriazine resin condensate is concentrated at 80°C to give a highly concentrated aminotriazine resin solution which has a solids content of 76% by mass and a butanol content of 3.1% by mass.

15 The highly concentrated solution of the etherified aminotriazine resin is subsequently mixed in a mixing zone with 0.8 kg of Simusol BPLE (oligoethylene glycol ether of bisphenol A), transferred to a second vacuum  
20 evaporator and concentrated at 90°C to give a syrupy melt which has a solids content of 98% by mass and a butanol content of 2.2% by mass.

2.2 Production of the prepreg and pressing to give the  
25 fiber composite

The syrupy melt is metered at 2.8 kg/h into the feed hopper of a GL 27 D44 (Leistritz) laboratory extruder having vacuum devolatilization zones after the feed  
30 zone and before the product discharge, sidestream metering for liquid media and 100 x 2 mm flat sheet die, temperature profile 180°C/220°C/220°C/220°C/200°C/170°C/140°C/ 110°C/90°C/90°C/90°C, extruder speed 200 min<sup>-1</sup>, the aminotriazine ether is subjected to  
35 thermal condensation and the volatile fractions are removed by devolatilization at 100 mbar.

The analysis sample of aminotriazine ether/polyamino-triazine ether mixture taken from the vacuum

devolatilization nozzle has a molar mass of 3800.

1.9 kg/h of tetramethylene diisocyanate are metered  
into the melt of the aminotriazine ether/polyamino-  
5 triazine ether mixture by means of sidestream metering  
and homogenized with the mixture. After a second vacuum  
devolatilization at 150 mbar, the melt is extruded  
through the flat sheet die onto a glass fiber fabric  
moving at 3.5 m/min (mass per unit area 200 g/m<sup>2</sup>), which  
10 fabric passes through a heating tunnel (120°C, average  
residence time 8 min) after the impregnation.

The impregnated glass fiber fabric has a resin content of 50% by mass. ATR investigations of the prepreg give a ratio of triazine sequence to carbamic ester groups of 1:3.7.

5

The impregnated glass fiber fabric is pressed in a press at 160°C/30 bar for 20 min with curing.

The laminate has the following material characteristics:

Flexural strength: 330 N/mm<sup>2</sup> Impact strength: 74 kJ/m<sup>2</sup>  
Tensile strength: 188 N/mm<sup>2</sup> Elongation: 2.8%.

If a laminate having the same resin content is produced under analogous conditions but without addition of the diisocyanate, the following material characteristics are obtained:

Flexural strength: 295 N/mm<sup>2</sup> Impact strength: 50 kJ/m<sup>2</sup>  
Tensile strength: 175 N/mm<sup>2</sup> Elongation: 2.0%.

20

### Example 3

For the production of the prepreg, 2,4,6-tris(methoxymethylamino)-1,3,5-triazine is used as the aminotriazine ether, bis(hydroxyethyl) terephthalate as the diol component for the transesterification and diisocyanatodiphenyl ether as the diisocyanate.

The transesterification and thermal autocondensation of the aminotriazine ether is carried out in a measuring kneader (from Haake Polylabsystem 540p). After preheating to 170°C, 32.5 g of bis(hydroxyethyl) terephthalate and 39.5 g of 2,4,6-tris(methoxymethylamino)-1,3,5-triazine are metered into the kneading chamber and kneaded at a speed of 50 min<sup>-1</sup> until a torque of 3 Nm is reached after a reaction time of 6 min. After cooling, the mixture of aminotriazine ether and polyaminotriazine ether is milled in a 100 UPZ/II universal mill (Alpine Hosokawa) with impact

disk and 2 mm sieve. GPC investigations give a molar mass of 1650.

5 50 g of the mixture of aminotriazine ether and polyaminotriazine ether are dissolved in 200 ml of dimethyl sulfoxide at 110°C, the solution is cooled to 50°C, 68 g of diisocyanatodiphenyl ether and 2 g of dibutyl phthalate are then added and the mixture is homogenized.

- The viscous solution is applied by means of a knife coater to a nonwoven cellulose web (120 g/m<sup>2</sup>, Lenzing AG, Austria), and the impregnated nonwoven cellulose is fixed in a needle bar frame and dried in a vacuum drying oven for 5 hours at 115°C/0.1 bar. The prepregs thus produced have a resin coat of about 50%. ATR investigations of the prepreg give a ratio of triazine sequence to carbamic ester groups of 1:3.
- 10 The prepregs are cut to a size of 30 x 20 cm. For the production of a shaped article having curved edges in the form of a U-profile, 3 prepregs plus an untreated nonwoven cellulose as the top are placed one on top of the other in a compression mold (30 x 20 cm) preheated to 160°C, and the press is slowly closed, the uncured prepregs being capable of being easily molded. Under pressure of 160 bar, the temperature is increased to 180°C and molding is effected for 20 min. The finished workpiece is removed and slowly cooled, and the flash formed by emerging resin at the immersion edge of the compression mold is ground off.
- 20 Test specimens cut out from the workpiece have, in the bending test, a modulus of elasticity of 6.5 GPa, an elongation at maximum force of 3.2% and an impact strength of 13 kJ/m<sup>2</sup>.